Studies On The Dielectric Behavior In (100-*x*) wt. % Methyl Cellulose (MC) + *x* wt. % NH_4NO_3 Polymer Electrolytes

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Abstract

This paper reports the dielectric behavior of (100-x) MC + x NH_4NO_3 (x=5, 10, 15, 20, and 30 wt. %) electrolyte system calculated using data from impedance measurement at roo temperature over the frequency range 50 Hz to 1 M Hz. The results obtained show th dielectric constant, dielectric loss, imaginary part of electrical modulus and loss tange shows changes with frequency. The dielectric properties of the samples at low frequenci have been explained on the basis of space charge polarization. The relaxation time for the samples is determined from the variation of loss tangent at different frequencies at roo temperature. The relaxation time decreases with conductivity of the complexes.

Keywords: methyl cellulose, ammonium nitrate, dielectric behavior

1. INTRODUCTION

There has been considerable interest on the study of the dielectric behavior in polymer electrolytes because it gives important information even though these materials have adequately high ionic conductivity [1]. By studying the dielectric behavior, some of the physical and chemical properties of the polymer can evaluate and the structure of material can be understood [2]. Ramesh et al. [3] stated that, studying the dielectric behavior help in understanding the conductive behavior of polymer electrolytes. Jang et al. [4] have studied the effect of chitosan concentration on the electrical property of chitosan-blended cellulose electroactive paper (CBC EAPap) and found that the relaxation time decreased while the ion mobility and the conductivity increased with increasing chitosan-blending ratios in CBC EAPap. The aim of investigating dielectric behavior of methyl cellulose (MC) doped with ammonium nitrate (NH_4NO_3) this work is to understand the conductivi behavior of the electrolyte films. Meth cellulose is used as polymer host a ammonium nitrate as the doping salt we used in this study because only lit attention has been paid to proton conducti polymer electrolytes using MC host. Oth ammonium salts used as proton donors a ammonium triflate ($NH_4SO_3CF_3$) [5- ammonium sulfate [$(NH_4)_2SO_4$] [7], tet methyl ammonium bromide [$(CH_3)_4$]N [8], ammonium thiocyanate (NH_4SCN) [10] and ammonium iodide (NH_4I) [11-12].

2. EXPERIMENTAL

2.1 Materials

Methyl cellulose (MC) from Sig Aldrich as polymer host, ammonium nitr (NH_4NO_3) from Ajax as salt and distil water as solvent.

2.2 Sample Preparation

Polymer electrolytes were prepared using solution casting technique. Samples were prepared using a general formula (100-x) wt. % MC + x wt. % NH_4NO_3 (x=5, 10, 15, 20, 25 and 30). MC was dissolved in distilled water and stirred until clear viscous solution. NH_4NO_3 was added accordingly and stirred again until 24 hours for solution completely dissolve. After complete dissolution, the solutions were cast in plastic petri dishes and left to dry at room temperature to form films.

2.3 Impedance Measurements

The solid (100-x) MC + x NH_4NO_3 electrolyte film were sandwiched between stainless steel and impedance measurements were performed with electrochemical impedance spectroscopy (HIOKI 3531-01-LCR bridge) that has been interfaced with a computer in the frequency range 50 Hz to 1 M Hz at room temperature. The dielectric constant, dielectric loss, imaginary part of modulus and loss tangent was calculated from the impedance data.

3. RESULTS AND DISCUSSION

3.1 Impedance Analysis

The impedance plot of 70 wt. % MC + 30 wt. % NH_4NO_3 at room temperature is shown in Fig. 1. The $-Z_i$ versus Z_r plots shows a straight line at lower frequency region and semicircular arc at the higher frequency region. The bulk resistance of the electrolyte film was taken from the intercept on the real X-axis at the higher frequency side.

The ionic conductivity of the samples was calculated using the equation as follows in Ref. 13-16.
The value of the bulk resistance and conductivity are tabulated in Table 1.

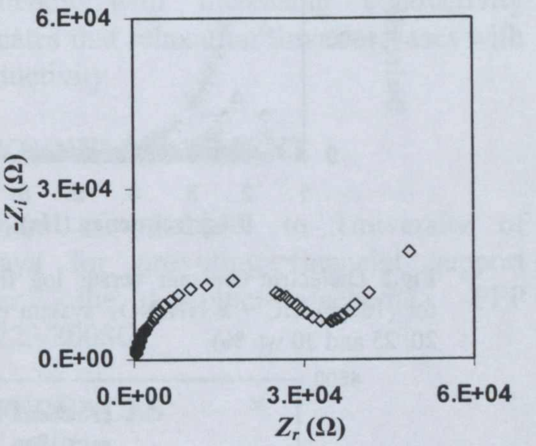

Fig. 1 Impedance plot of 70 wt. % MC + 30 wt. % NH_4NO_3.

The value of R_b for the samples is decrease with addition of NH_4NO_3. This implies that the conductivity has increase with addition of NH_4NO_3. The conductivity of the system was optimized for sample containing 25 wt. % salt.

3.2 Dielectric Behavior

The effect of NH_4NO_3 concentration on the frequency-dependent dielectric behavior of (100-x) MC + x NH_4NO_3 system was analyzed using the equation as follows in Ref. 17-19.

3.2.1 Dielectric loss and dielectric constant

Fig. 2 and 3 shows the variation of dielectric constant, ε_r and dielectric loss, ε_i as a function of frequency for MC-NH_4NO_3 complexes at room temperature.

TABLE 1. The values of bulk resistance, R_b and conductivity, σ of samples with respective composition

(100-x) wt. % MC + x wt. % NH_4NO_3	Bulk resistance, R_b (Ω)	Conductivity, σ (S cm^{-1})
100 wt. % MC	4.31 x 10^7	3.08 x 10^{-11}
95 wt. % MC + 5 wt. % NH_4NO_3	2.52 x 10^6	6.74 x 10^{-10}
90 wt. % MC + 10 wt. % NH_4NO_3	5.41 x 10^5	2.49 x 10^{-9}
85 wt. % MC + 15 wt. % NH_4NO_3	3.74 x 10^4	5.75 x 10^{-8}
80 wt. % MC + 20 wt. % NH_4NO_3	6.43 x 10^3	3.10 x 10^{-7}
75 wt. % MC + 25 wt. % NH_4NO_3	7.81 x 10^2	2.10 x 10^{-6}
70 wt. % MC + 30 wt. % NH_4NO_3	3.35 x 10^4	6.40 x 10^{-8}

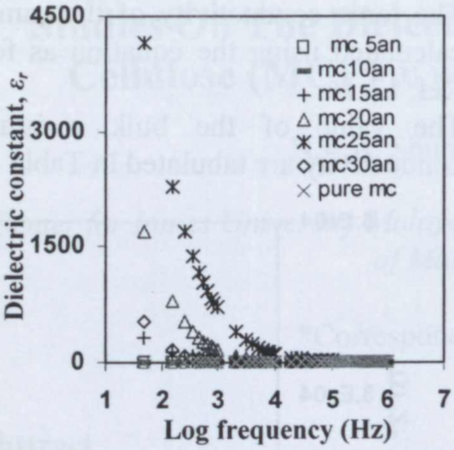

Fig.2 Dielectric constant versus log frequency plot for (100-*x*) MC + *x* NH_4NO_3 system (*x*= 5, 10, 15, 20, 25 and 30 wt. %)

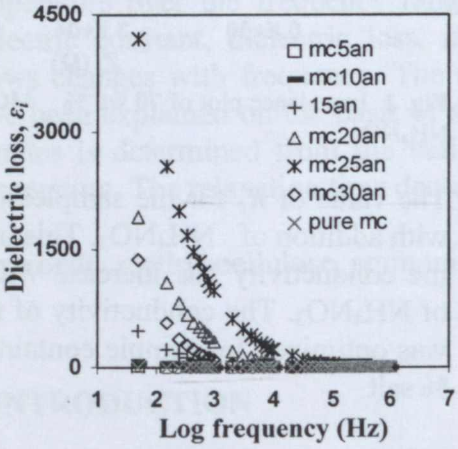

Fig. 3 Dielectric loss versus log frequency plot for (100-*x*) MC + *x* NH_4NO_3 system (*x*= 5, 10, 15, 20, 25 and 30 wt. %).

It can be seen that the value of ε_r and ε_i decrease with increasing the frequency up to 10^6 Hz. The decrease in the value of ε_r and ε_i may be attributed to the electrical relaxation process [20] and indicating that electrode polarization due to charge accumulation has taken place in space [21-22]. Baskaran et al. [23] reported that, non-Debye behavior was happen because the formation of space charge regions at the electrode-electrolyte interfaces at low frequencies. At high frequencies, the periodic reversal of the electric field occurs at the interface, the contribution of mobile ions towards ε_r decreases with increasing frequency.

In the both of the figures, no appreciable relaxation peaks are observed in the studied frequency range. These shows the increase in conductivity is due to an increase in the number density of mobile ions. The variation in ε_r and ε_i are observed follow t same trends as in the conductivi composition relationship. The sample h the highest conductivity value has t highest dielectric constant and dielect loss.

3.2.2 Real And Imaginary Part Of Electri Modulus.

Depicted in Fig. 4 is the variation imaginary (M_i) part of the electri modulus at room temperature for the vario concentration of NH_4NO_3 salt.

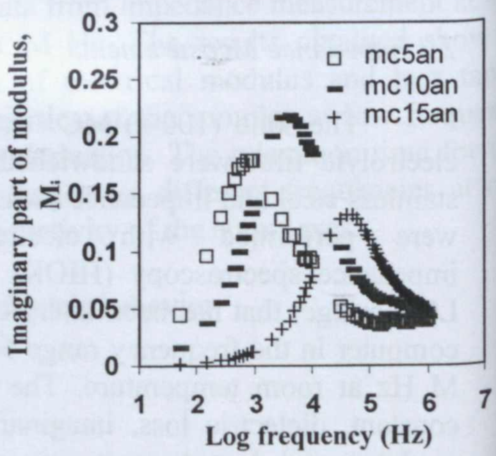

Fig. 4 Imaginary part of modulus, M_i log frequency for (100-*x*) MC + *x* NH_4NO_3 system (*x*= 5, 10, 15, 20, and 30 wt. %).

The existence of a long tail at the lo frequency end is attributed to the la capacitance associated with the electro [18]. In M_i versus log frequency plots, appearance of peaks which correspond the conductivity relaxation [20] observed to shift from low to hig frequency region and it follows the trend the conductivity variation [24]. T presence of such peaks in M_i plots indica that the electrolyte system is an io conductor [21].

3.2.3 Loss Tangent

Fig. 5 depicts the frequency dependence loss tangent at room temperature. T angular frequency of the applied field, ω which the $(\tan\delta)_{max}$ occurs, the relaxati time for the ionic charge carriers, τ can calculated by the relation:

$$\tau\omega = 1 \quad (1$$

where ω is the angular velocity, $\omega = 2\pi f$, f is the frequency value corresponding to maximum tan δ.

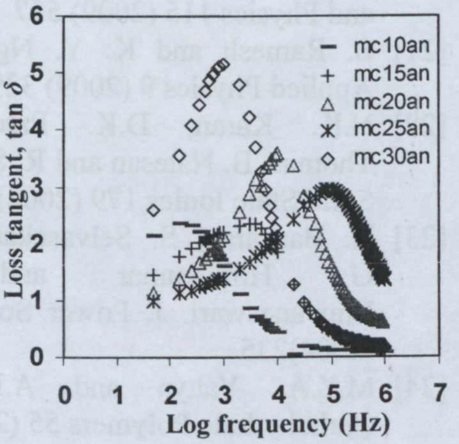

Fig. 5 Loss tangent versus log frequency plot for (100-x) MC + x NH_4NO_3 system (x= 5, 10, 15, 20, 25 and 30 wt. %)

The occurrence of relaxation time is the result of the efforts carried out by ionic charge carriers within the polymer material to obey the change in the direction of applied field. The shift of $(\tan \delta)_{max}$ towards higher frequency with increasing conductivity indicates that relaxation time decrease with conductivity as shown in Fig. 6.

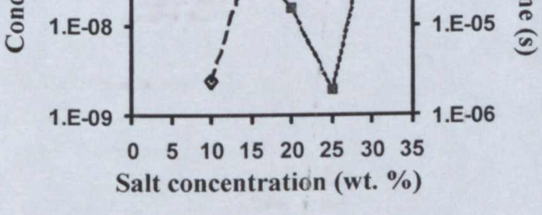

Fig. 6 The dependence of conductivity and relaxation time on NH_4NO_3 salt concentration at room temperature

4. CONCLUSIONS

The value of dielectric constant, ε_r and dielectric loss, ε_i of (100-x) MC + x NH_4NO_3 (x = 5, 10, 15, 20, 25 and 30 wt. %) electrolyte films are decreased with frequency is attributed to the polarization due to the charge accumulation. The presence of such peaks in M_i plots shows the electrolyte system is ionic conductor. The $(\tan \delta)_{max}$ are shifted from lower to higher frequency with increasing conductivity indicates that relaxation time decreases with conductivity.

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REFERENCES

[1] K. Pandey, M.M. Dwivedi, M. Singh and S.L. Agrawal. J. Polym. Res. DOI10.1007/s10965-009-9298-3

[2] I. M. El-Anwar, O.M. El-Nabawy, S.A.El-Hennwii and A.H. Salama.Chaos, Solitons and Fractals 11 (2000)1301

[3] S. Ramesh, A.H. Yahya and A.K. Arof. Solid State Ionics 152-153 (2002) 291

[4] S-D. Jang, J-H. Kim, C. Zhijiang and J. Kim. Smart. Mater. Struct 18 (2009)015003

[5] S. Chintapalli, C. Zea and R. Frech. Solid State Ionics 92 (1996) 205

[6] R. Kumar, J.P. Sharma and S.S. Sekhon. European Polymer Journal 41 (2005) 2718

[7] A.M.M. Ali, N.S. Mohamed and A.K. Arof. J. Power Sources 74 (1998) 135

[8] D.S. Reddy, M.J. Reddy and U.V.S. Rao. Materials Science and Engineering B78 (2000) 59

[9] C.S. Ramya, S. Selvasekarapandian, T. Savitha, G. Hirankumar, R.Baskaran,M.S. Bhuvaneswari and P. C. Angelo. European Polymer Journal 42 (2006) 2672

[10] S. Selvasekarapandian, R. Baskaran, and M. Hema. Physica B 357 (2005)412

[11] K.K. Maurya, N. Srivastava, S.A. Hashmi and S. Chandra. J. Materials Science 27 (1992) 6357

[12] M.H. Buraidah, L.P. Teo, S.R. Majid

and A.K. Arof. Physica B 404 (2009) 1373

[13] V. Raja, A.K. Harma and V.V.R. Narasimha Rao. Materials Letters 58 (2004) 3242

[14] M.J. Reddy and P. P. Chu. Electrochim. Acta 47 (2002) 1189

[15] X. Qian, N. Gu, Z.Cheng, X. Yang, E. Wang and S. Dong. Electrochim. Acta 46 (2001) 1829

[16] N.S. Mohamed, M.Z. Zakaria, A.M.M. Ali and A.K. Arof. J. Power Sources 66 (1997) 69

[17] A.S.A. Khiar, R. Puteh and A.K. Arof. Physica B 373 (2006) 23

[18] Z. Osman, Z.A. Ibrahim and A.K. Arof. Carbohydrate Polymers 44 (2001) 167

[19] S. R. Majid and A. K. Arof. Physic 390 (2007) 209

[20] D.K. Pradhan, R.N.P. Choudhary B.K. Samantaray. Materials Chemi and Physics 115 (2009) 557

[21] S. Ramesh and K. Y. Ng. Curr Applied Physics 9 (2009) 329

[22] N.K. Karan, D.K. Pradhan, Thomas, B. Natesan and R. S. Kati Solid State Ionics 179 (2008) 689

[23] R. Baskaran, S. Selvasekarapandi G. Hirankumar and M Bhuvaneswari. J. Power Sources (2004)235

[24] M.Z.A. Yahya and A.K. A Carbohydrate Polymers 55 (2004) 9